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## **(54) PHOTOGRAPHIC COLOR DEVELOPER COMPOSITION AND DEVELOPING METHOD**

### **(57)Abstract:**

**PROBLEM TO BE SOLVED:** To obtain a color developer compsn. for a color photographic sensitive material contained in a plastic vessel, excellent in shelf stability, having a single liq. agent structure which does not require mixing and dissolution work in a processing laboratory and enabling the recycling of the used vessel.

**SOLUTION:** A replenisher liq. agent for color development having a specific gravity of 1.15-1.30, contg. 4-amino-3-methyl-N-ethyl-N-( $\beta$ -methanesulfoamidoethyl) aniline or its salt as a color developing agent and contg. all the constituent components of a development replenisher soln. in a single solvent is filled into a vessel comprising a single material and having 413 ml/24 hr.atm/l oxygen permeation rate to obtain the objective color developer compsn. for a silver halide color photographic sensitive material.

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## **CLAIMS**

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**[Claim(s)]**

[Claim 1] Specific gravity is in the range of 1.15-1.30, and contains a 4-amino-3-methyl-N-ethyl-N-(beta-methane sulfo amide ethyl) aniline or its salt as a color development chief remedy. And the replenisher agent for the color developments which contains all the constituents of a development replenisher in single liquids and solutions The color development agent constituent for photographs characterized by the oxygen transmission rate which consisted of single ingredients coming to fill up the container of 4-13ml/(24hr.atm.l) (per unit volume of contents liquid [ in / at the temperature C of 25 degrees / 50% of relative humidity ]).

[Claim 2] The color development agent constituent according to claim 1 characterized by coming to fill up polyolefin resin the container made as a single component.

[Claim 3] The color development agent constituent according to claim 1 or 2 characterized by the thing of the alkanolamine further chosen from the group of the following general formula [A] into a constituent included for one at least.

[H(R'O) m R] n NH (3-n) [A]

(0 or 1, and n of m are the integers of 1-3 among a formula [A], and, as for the hydroxy permutation alkylene group of 2 to 4, and R', a carbon number is [ the carbon number of R ] the alkylene group or hydroxy permutation alkylene group of 1-4.) However, when m is 0, if n is 2 if the carbon number of R is 2, and the carbon numbers of R are 3-4, n is 1, 2, or 3. Moreover, when m is 1, it is not based on the class of R but n is 1, 2, or 3.

[Claim 4] The color development agent constituent according to claim 1 to 3 characterized by containing a polyalkylene glycol in a constituent.

[Claim 5] The development approach of the silver halide color photography sensitive material characterized by performing color development processing for the exposed silver halide color photography sensitive material using a color development agent constituent according to claim 1 to 4.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

## [0001]

[The technical field to which invention belongs] This invention relates to the development approach by the auto-processor using the color development agent constituent for color photography sensitive material and it with specifically high the handling nature, transport fitness, and preservation stability which were contained by the container with few environmental loads about the development approach using the color development agent and it which are used for processing of silver halide color photography sensitive material.

## [0002]

[Description of the Prior Art] Generally processing of silver halide photosensitive material, for example, processing of silver halide color photography sensitive material, consists of image stabilization processes, such as a color development process, a desilvering process, and rinsing, as a basic process. At a color development process, image-like coloring matter and image silver generate by the reaction of a color development chief remedy and silver salt. At a desilvering process, the image silver produced at the color development process oxidizes to silver salt with the bleaching agent which has the oxidation (bleaching), and is removed from a sensitization layer by the fixing agent which forms fusibility silver with a still more nearly intact silver halide. Or the oxidation and its clearance to silver salt are performed by the bleach fix bath by the single step. An image stabilization process is a process at which accommodation of the ambient atmosphere of an image layer is made, in order to secure the stability over the long period of time of the generated image, and either rinsing or rinsing, an image stability bath or the stable bath replaced with rinsing is performed. Each down stream processing is performed using the water solution (it is called processing liquid) containing one or more kinds of processing chemicals, if rinsing is removed. Since each processing liquid is low concentration comparatively, generally it is unsuitable from a viewpoint of the financial side, a storage-space side, or a working plane for a processing chemical manufacturer to manufacture the processing liquid in the condition that it can be used as it is, to convey it to a processing laboratory, and to keep it.

[0003] Conventionally, two kinds of approaches were carried out to solution of this problem. One supplies the so-called \*\*\*\* of the solid-state processing agent which prepared the dry-chemicals mixture which mixed the processing chemical which constitutes processing liquid by the ratio according to a processing liquid configuration, and packed it to a processing laboratory. It is the method which dissolves it in water in a processing laboratory, dilutes to suitable concentration, and is used as processing liquid. Another is a method which dilutes to the concentration which supplied the processing laboratory in the form of the thick liquid processing agent with which dissolved the configuration processing chemical in high concentration, changed into the liquefied thick condition, and the container was filled up, and was able to define it in the processing laboratory with water etc., and is used for it as processing liquid. The former is described at U.S. Pat. No. 2843484, 2846308, the Canada patent 831st, No. 928, etc., and the latter is describing the thick liquid processing agent for color development at U.S. Pat. No. 3574619, 3647461, 3814606, and the open British patent specification No. 2016723. Although

it changes with magnitude of a processing laboratory etc., any are advantageous In the small-scale processing laboratory called the mini-laboratory, micro lab, or shop front lab which has increased recently As for the engineer who became skilled, it is common that it does not break but there is also no full-scale equipment. Under such a working condition Since solid processing agents, such as powder, granulation, and a tablet, have the slow dissolution rate, it is necessary to use the warm water around 40 degrees C, and to dissolve, and it is the gestalt which is very hard to treat, and the warm water supply equipment for it and a stirring facility are also needed. On the other hand, also in chilled water, it is easily mixable, and since warm water supply equipment and the special stirring facility are unnecessary, the liquid processing agent is convenient to a small-scale processing laboratory, and is usually used for a target.

[0004] However, a liquid processing agent has the fault to which air oxidation of the component is easy to be carried out, and both components also tend to react. Therefore, in order to prevent this and to secure prolonged preservation stability, a liquid processing agent is divided into two or more PERT, or it contains in the low container of oxygen permeability, and the means of preventing oxidation are taken. Especially, when stability is the color development agent thought most as important, usually it is made the liquid processing agent divided into three of preservatives PERT, such as alkali-chemicals PERT, color development chief remedy PERT, and a hydroxylamine.

[0005] However, in small-scale processing laboratories, such as a mini-laboratory, preparation of processing liquid is also performed by the person non-become skilled in many cases, and the processing agent divided into two or more PERT tends to cause a mixing mistake. In order to constitute the color development agent of a liquid from single part in JP,63-17453,A in order to cancel this fault, and to secure preservation stability, the approach of containing in containers with which both the steam transmission rate and the oxygen transmission rate used the low ingredient, such as a polyvinyl chloride, polyethylene terephthalate, and nylon, is indicated. By this, even after saving the liquid color development agent constituted from single part for ten months in ordinary temperature, it maintains the ullage of enough color development chief remedies, and it is indicated that the good photograph engine performance was secured.

[0006] Although the technique indicated by the above-mentioned official report is effective in stability reservation of a color development chief remedy to be sure, even if it carries out with this technique, neither from the preservation under the elevated temperature exceeding 30 degrees C of a summer, nor that for ten months or more, in prolonged preservation, a sulfite decreases, and it turns out that high-contrast-izing of the photograph engine performance and fluctuation of fogging break out, and it can be said that it has still satisfactory stability. Moreover, it cannot be said that the stability over the strong-base nature liquids and solutions of a container ingredient is also enough.

[0007] As a container which can prevent air oxidation nearly thoroughly, although glassware was used for some time, there is risk of breakage, it was dealt with and the sex was inconvenient. Subsequently, although the container of the ingredient with which oxygen permeability carried out the laminating of the stable plastic material to low plastic material and development liquid was used, it was the demerit on environmental protection cost is not only high, but that cannot carry out the playback activity of the used container. It is desired from a viewpoint of environmental protection for a playback activity to be possible, and it is required to be made from a single component for that purpose. Although there are polyester, nylon, etc. in the low plastic ingredient of oxygen permeability with the single ingredient in which a playback activity is possible, neither has sufficient stability chemically to the development agent of strong-base nature. On the other hand, although there are polyolefines, such as polyethylene and polypropylene, in the single ingredient in which a stable playback activity is possible to development liquid, there is a difficulty that oxygen permeability cannot prevent air oxidation greatly.

[0008] Furthermore, in order to perform an economic burden for a reuse few, it is making a container thin and decreasing the quantity of the ingredient itself, and that especially a thing for which a used container can be crushed and reduced simultaneously is desired. In the case of a polyethylene bottle or a polypropylene bottle, the concrete plastic envelope which fulfills such demand characteristics is much more unsuitable for preservation of the processing liquid which oxygen permeability becomes still larger

as for the container of such thin thickness, and is easy to receive oxidation like a developer, although thickness is 1mm or less. Therefore, a playback activity is possible and the container for development agent constituents with oxygen permeability low enough is stably demanded strongly to the development constituent. In addition, it means that the vocabulary "a playback activity" in this description reproduces and uses a used container for a new container through a recycle process, and adds that it is not the "reuse" which carries out periodic duty of the same container by way of precaution.

[0009]

[Problem(s) to be Solved by the Invention] Therefore, the function needed about the color development constituent of a container restoration mold (1) About an environmental load, are the ingredient in which a playback activity is possible, and the material of construction is little, and it is sufficient for it, and is related with that there are few loads of a recycle process, and (2) development working plane.

Preparation (preparation) actuation of processing liquid is related with the engine performance of that it is unnecessary and handling nature is good and (3) processing liquid. Without processing liquid and a processing agent container also coloring it the retention period over a long period of time according to air oxidation, a non-melt's depositing, or the oil of tar nature dissociating, it is maintained by stability, without the photograph engine performance also deteriorating, and implementation of these functions is demanded.

[0010] It is the single liquids-and-solutions configuration which is the technical problem in which filling the above-mentioned want tends to solve this invention, namely, the 1st object of this invention excels [ configuration ] in preservation stability, and moreover does not need a mixed dissolution activity in a processing laboratory, and is offering the color development agent constituent for the color photography sensitive material of entering [ in which the playback activity of a used container is possible ] a plastic envelope. The 2nd object of this invention is simple for the actuation which used the above-mentioned liquid thick developer constituent containing a plastic envelope, and it is offering the color development approach quality's being maintainable to stability.

[0011]

[Means for Solving the Problem] this invention person reached this invention, as a result of repeating examination wholeheartedly to the above-mentioned object, discovering the unique phenomenon in which an oxidation rate with the air penetrated from the container outside decreases and repeating examination about the relation of this phenomenon and the oxygen transmission rate of a plastic envelope further based on this discovery, when the liquid development agent constituent in the condition that the plastic envelope was filled up has a certain specific specific gravity value. That is, the object of this invention is reached by the specific combination of the conditions of the following plastic envelopes, and the conditions of the liquid thick processing agent constituent for the color developments.

[0012] 1. Specific Gravity is in the Range of 1.15-1.30, and Contains 4-Amino-3-Methyl-N-Ethyl-N-(Beta-Methane Sulfo Amide Ethyl) Aniline or Its Salt as a Color Development Chief Remedy. And the replenisher agent for the color developments which contains all the constituents of a development replenisher in single liquids and solutions The color development agent constituent for photographs characterized by the oxygen transmission rate which consisted of single ingredients coming to fill up the container of 4-13ml/(24hr.atm.l) (per unit volume of content liquid [ in / at the temperature C of 25 degrees / 50% of relative humidity ]).

[0013] 2. Color development agent constituent given in the above 1 characterized by coming to fill up polyolefin resin container made as single component.

[0014] 3. The above 1 characterized by thing of alkanolamine further chosen from group of following general formula [A] into constituent included for one at least, or color development agent constituent given in 2.

[H(R'O) m R] n NH (3-n) [A]

(0 or 1, and n of m are the integers of 1-3 among a formula [A], and, as for the hydroxy permutation alkylene group of 2 to 4, and R', a carbon number is [ the carbon number of R ] the alkylene group or hydroxy permutation alkylene group of 1-4.) However, when m is 0, if n is 1, if the carbon number of R

is 2, and the carbon numbers of R are 3-4, n is 1, 2, or 3. Moreover, when m is 1, it is not based on the class of R but n is 1, 2, or 3.

[0015] 4. Color development agent constituent given in either of the above 1-3 characterized by containing polyalkylene glycol in constituent.

[0016] 5. Development approach of silver halide color photography sensitive material characterized by performing color development processing using color development agent constituent given [ silver halide color photography sensitive material ] in either of the above 1-4.

[0017] In addition, the method of equipping with a color development agent constituent the auto-processor automatically supplemented with a replenisher, and performing color development processing also in the above-mentioned development approach using the color development agent constituent of this invention, is a desirable mode in which the effectiveness of this invention shows up notably especially. After equipping with the container which filled up the auto-processor with the color development agent constituent and pouring in the contents of this container into a development supplement tub also in it, while the water of a constant rate washes the inside of a container the water used for washing -- the inside of a supplement tub -- introducing -- preparation of a replenisher -- the development approach of silver halide color photography sensitive material of using it as service water and performing a development using the obtained replenisher is a mode which demonstrates the advantage of this invention, and the detail is described later.

[0018]

[Embodiment of the Invention] The gestalt of the operation of this invention to the following is explained to a detail. This invention relates to the configuration and stowage container of a liquid thick developer constituent for color photography sensitive material. (1) Specific gravity is in the range of 1.15-1.30. As a (2) color-development chief remedy 4-amino-3-methyl-N-ethyl-N-(beta-methane sulfo amide ethyl) aniline, Or salts, such as the chloride, a sulfate, and a p-toluenesulfonic-acid salt, are contained. (3) the replenisher agent for the color developments which contains all the constituents of a replenisher in single part (4) Consisted of single raw materials. (5) It is the color development agent constituent for silver halide color photography sensitive material characterized by coming to fill up an oxygen transmission rate the container of 4 - 13ml/(24hr.atm.l) (per unit volume of content liquid [ in / at the temperature C of 25 degrees / 50% of relative humidity ]).

[0019] Although the specific gravity of the usual color development replenisher is about 1.05, it is the indispensable requirements on the manifestation of the invention effectiveness to set the specific gravity of the color development agent constituent for preparing that replenisher to 1.15-1.30 in this invention, in the range of this specific gravity value, it is hard to receive air oxidation, therefore a reduction of the preservatives in a component or a color development chief remedy with time is prevented. Even if a specific gravity value is lower than this field and it is high, degradation of the constituent by air oxidation increases. That is, when a specific gravity value is lower than this range, reduction of the concentration of the preservatives by air oxidation or a color development chief remedy becomes remarkable, when higher than this range, a tar-like separation object will carry out coloring contamination of a developer, a container, or the developing-machine wall, and the oxidized color development chief remedy will degrade a developer constituent anyway. The range where a specific gravity value is desirable is 1.18-1.27, and is 1.18-1.24 more preferably.

[0020] As for the concrete means which raises a specific gravity value to this range, it is simplest to raise the enrichment of a constituent. It is effective that solubility chooses a compound with few adverse effects to photograph nature as a constituent greatly relatively in the compound group of these functions, such as to use potassium carbonate for alkali chemicals and to use potassium chloride for a chloride in order to avoid that solubility restrains and a component deposits, in case enrichment is raised. Moreover, they are the large carbonic acid alkali of the contribution to specific gravity, and the means which can be taken in in the range which the photograph engine performance allows also in making many potassium carbonate contain and enlarging specific gravity also in it among alkali chemicals, such as carbonic acid alkali in a constituent, a potassium hydroxide, and a sodium hydroxide. Moreover, for the object of only specific gravity accommodation, it may not have buffer capacity in the nine to pH12 neighborhood, but

alkali soluble an inorganic-acid salt or an organic-acid salt which is stated to the next with little effect also at the photograph engine performance may be added. Moreover, it is also desirable this and to add the dissolution assistant which raises solubility so that it may state below.

[0021] As an example of a dissolution assistant desirable in order to raise the solubility of each component, when using a water-soluble dissolution assistant Alcohols, such as methyl alcohol, ethyl alcohol, propyl alcohol, and isopropyl alcohol, Ethylene glycol, a diethylene glycol, triethylene glycol, Glycols, such as a with a molecular weight of 6000 or less polyethylene glycol Alkanolamines, such as diethanolamine and triethanolamine, Para toluenesulfonic acid sodium, and a PARATORUE potassium are desirable, and a diethylene glycol and a Para toluenesulfonic acid salt are especially desirable.

[0022] Moreover, it is also desirable to add sodium salt and potassium salt of a chelating agent, such as the sodium carbonate and potassium carbonate which are known as a component of color development liquid or a color development replenisher, other ethylenediaminetetraacetic acid, a diethylenetriamine pentaacetic acid, the 1-hydroxy ethylidene 1, 1-diphosphonic acid, hydroxy ethylimino 2 acetic acid, nitrilotriacetic acid, ethylenediamine 4 methylene phosphonic acid, and nitrilotrimethylenephosphonate, more than the usual quantitative ratio with other components, and to raise specific gravity.

[0023] A compound with still less effect for the engine performance of color development liquid can be added, and specific gravity can also be adjusted. Organic acids, such as an acetic acid besides alkali-metal sulfates and alkali-metal chlorides, such as a sodium sulfate, potassium sulfate, a sodium chloride, and potassium chloride, oxalic acid, a citric acid, a maleic acid, succinic acid, a product from a tartar, a product from a horse mackerel pin, a glycolic acid, a lactic acid, and a glutaric acid, may be made to contain in the form of sodium salt, potassium salt, or lithium salt as an example of such a specific gravity modifier. In addition, JP,6-02627,A may be made to contain various kinds of monosaccharides of a publication. Moreover, sulfinic acids given in JP,1-224762,A, such as a PARATORU en sulfinic acid and a meta-carboxy sulfinic acid, and the salt of those can also be made to contain. In the above specific gravity modifier, a sulfate, sulfinate, soluble starch, and saccharose are desirable.

[0024] Although the mechanism of action of the effectiveness of specific gravity accommodation of this invention is not clear, change of the rate of absorption to the processing agent of the oxygen in air or a carbon dioxide and the reaction rate between processing agent components combines, and what produces the optimal effectiveness in the specific gravity range of this invention is presumed.

[0025] Although it is dependent on the presentation of the developer to be used, in many cases, a concentration rate required to make specific gravity into this range is the 1.5 to 10 times as much range as a developer, more generally is two to 8 times, and becomes three to 8 times at many developers for \*\*. In addition, the enrichment in this case means the dilution scale factor at the time of preparing a development replenisher by dilution from a constituent.

[0026] In the case of salts, such as a 4-amino-3-methyl-N-ethyl-N-(beta-methane sulfo amide ethyl) aniline and its chloride, a sulfate, and a p-toluenesulfonic-acid salt, the color development chief remedy is accepted, therefore, as for effectiveness being in this specific specific gravity range, these color development chief remedies are used for this invention. Especially desirable color development chief remedies are 4-amino-3-methyl-N-ethyl-N-(beta-methane sulfo amide ethyl) aniline 3 / disulfuric acid salt 1 hydrate in it.

[0027] Moreover, the development agent constituent of this invention makes the workability of a processing laboratory simple by including all the constituents of a replenisher in single configuration liquids and solutions also in combination of a component to which oxidation will progress if it lives together like a color development chief remedy and alkali chemicals, without dividing into another configuration liquids and solutions. Therefore, it is desirable to contain the preservatives which raise preservation and stability, a dissolution assistant, and distributed assistants in a developer constituent. As explaining in full detail behind, the concrete addition compound explains a container first.

[0028] The oxygen transmission rate of the container which consisted of single ingredients used by this invention is 4-13ml/(24hr.atm.l) per 1l. of internal solutions, is 5-12ml/(24hr.atm.l) per 1l. of internal solutions preferably, and is 6-10ml/(24hr.atm.l) more preferably. This value may only be called an oxygen transmission rate, when it is the value broken by the volume (liter) of the developer constituent

with which the exterior of a container is filled up per unit volume of the condition of anoxia (nitrogen-gas-atmosphere mind), and with the amount of oxygen transparency per 24 hours by the oxygen of one atmospheric pressure, and a container is filled up with the interior and there is only no risk of misunderstanding. In the container exterior, the interior carries out the quantum of the measurement of an oxygen transmission rate using oxygen or air with the gas-chromatography equipment of marketing of the oxygen density which fills nitrogen gas and is penetrated inside. When the external ambient atmosphere at the time of measurement is air, the oxygen pressure of a container external environment is computed as oxygen tension of air.

[0029] Although it is natural when the oxygen transmission rate of a container exceeds the upper limit of the above-mentioned range, air oxidation becomes remarkable and degradation of a constituent becomes quick. Conversely, when lower than the minimum of the above-mentioned range, it means using a container ingredient more than an initial complement, and inconvenience produces that the load of a recycle process increases, that the cost in a transport supply process also increases, the thing that it is hard to reduce a used container (it is hard to crush) in respect of each.

[0030] As already stated, a playback activity is easy, and the container ingredient suitable for the object of this invention is chemically stable also to a developer constituent, and needs to be the raw material which can save a developer constituent at stability to it. The desirable container ingredients for color development agent constituents which fill this demand are polyamide resin, such as polyester resin, acrylic resin, ABS plastics, an epoxy resin, and nylon, polyurethane resin, polystyrene resin, polycarbonate resin, PVA, a polyvinyl chloride, Pori chlorination BINICHIDEN, and polyethylene resin, and the ingredient which suits especially the object of this invention also in it is an ingredient which constitutes a container for polyolefin resin, such as polyethylene and polypropylene, as single polymeric materials. Also in it, polyethylene \*\*\*\*\* HDPE of a high density mold is desirable as a container ingredient. The consistencies of HDPE suitable for a container ingredient are 0.94-0.97.

[0031] Since polyethylene and polypropylene had large oxygen permeability, it was thought that it was unsuitable as a container ingredient for developer constituents. However, in this invention, as a result of finding out that air oxidation is controlled by adjusting the specific gravity of a developer constituent in the above-mentioned range, it makes it possible polyolefin resin, such as large polyethylene of oxygen permeability, and polypropylene, and to especially use high density polyethylene (henceforth referred to as HDPE). Furthermore, in order to perform an economic burden for a reuse few, it is making a container thin and decreasing the quantity of the ingredient itself, and that especially a thing for which a used container can be crushed and reduced simultaneously is desired. Although thickness was 0.3-0.7mm, preservation of the developer constituent with which a container with such thin thickness also tends to receive oxidation of the concrete container which fulfills such demand characteristics was attained by adjusting the specific gravity of a polyethylene bottle, a polypropylene bottle, or the constituent with which it fills up in the aforementioned range.

[0032] In addition, although the example which contains a color development agent in a polyethylene container is indicated by JP,9-311425,A about the color development agent constituent of a thick liquid if it adds for a sense, the specific gravity of this processing agent constituent is lower than the minimum of the convention range of this invention, and specific gravity does not have the publication which suggests the knowledge of this invention of influencing the stability over air oxidation.

[0033] Moreover, although the example of a presentation in which specific gravity is presumed to be within the limits of this invention is looked at by the example of JP,6-230545,A about the auto-processor for silver halide sensitive material, there is no publication about a container in it, and there is also no publication about the stability of the processing agent constituent of the example of a presentation in it. Therefore, the knowledge found out by this invention is not suggested even if it combines also from each of the well-known example relevant to these color development agent constituents or them.

[0034] Although the requirements for a configuration and background briefing of this invention were performed above, the still more concrete mode of this invention is explained below. The constituent of the processing agent constituent of this invention is explained further first. Although the specific gravity

of a developer constituent is adjusted and the large polyolefine bottle of air permeability is made usable in this invention as stated previously, the constituent of said specific gravity within the limits is further made stability by adding preservatives, a specific dissolution assistant, or a specific distributed assistant in a constituent.

[0035] One of them is the alkanolamine chosen from the group of the following general formula [A], and it can heighten effectiveness further by [ the ] including one at least. Addition of alkanolamines has the effectiveness which inhibits both coloring of precipitation, a constituent, and a bottle. Effective alkanolamines are [ 0 or 1, and n of m ] 1-3 in a general formula [A], and, as for the straight chain of 2 to 4 or the hydroxy permutation alkylene group of branching, and R', a carbon atomic number, such as hydroxy ethylene and an n-hydroxy propylene radical, is [ carbon atomic numbers of R, such as a methylene group ethylene, n-propylene radical, and hydroxy ethylene, ] the straight chains, branching alkylene groups, or hydroxy permutation alkylene groups of 1-4. However, when m is 0, if n is 2 if it is the carbon atomic number 2 of R, and the carbon atomic numbers of R are 3-4, n is 1, 2, or 3. Moreover, when m is 1, it is not based on the class of R but n is 1, 2, or 3.

[0036] Effective alkanolamines are especially shown below also in it.

A-1 Tri-isopropanolamine, A-2 Diisopropanolamine, A-3 Monoisopropanolamine, A-4 Diethanolamine, A-5 2, 3-dihydroKISHIRU propylamine, A-6 A JI (2, 3-dihydroKISHIRU propyl) amine and A-7 JI (4-butanol) amine.

Especially effective alkanolamines are tri-isopropanolamine, diisopropanolamine, and diethanolamine. Even if it becomes excessive [ an alkyl part ] as effective alkanolamines have the suitable balance of a hydrophilic radical and a hydrophobic radical, and hydrophobicity increases to the object of this invention, even when a hydrophilic part is conversely excessive, there is little effectiveness. For example, as for the triethanolamine which is a well-known organic solvent for developer addition, effectiveness is not conventionally accepted in the object of this invention.

[0037] The addition of the above-mentioned alkanolamines is 0.02-3 mols per 1l. of processing agent constituents, and is 0.1-1 mol still more preferably 0.05-2 mols preferably.

[0038] Next, the polyalkylene glycol preferably used by this invention is explained in more detail. A desirable polyalkylene glycol is the block copolymer of a polyethylene glycol and a polyethylene glycol, and a polypropylene glycol. Molecular weight is the thing of 62-1500, \*\*\*\*\* spread more preferably is the thing of 100-800, and the thing of \*\*\*\*\* of 200-500 is [ a desirable polyethylene glycol ] good also in it. Moreover, the weight ratio to which molecular weight occupies the block copolymer of desirable ethylene glycol propylene glycol to the copolymer of an ethylene glycol unit by 200-2000 is 50 - 95% of thing, and the weight ratio which molecular weight occupies to the copolymer of an ethylene glycol unit by 300-1000 more preferably is 50 - 80% of thing. In addition, although it is needless to say, each above-mentioned molecular weight is average molecular weight (a number average or a weighted mean is not asked).

[0039] The addition of a polyalkylene glycol has the desirable range of 1.0-100g/l., and it is the range of 5.0-50g/l. more preferably.

[0040] In this invention, a high-concentration color development chief remedy can be further maintained at stability by adding the benzenesulfonic acid which may carry out alkylation, or its salt to a developer constituent. Especially, contamination by coloring of the constituent by the passage of time of a developer constituent and its container and adhesion in the sensitive material of the coloring object can be prevented or mitigated. Benzenesulfonic acid, the benzenesulfonic acid by which alkylation was carried out, or these salts are referred to as "carrying out alkylation" here. Moreover, it is desirable not to have any substituents other than an alkyl group and a sulfonic group. The number of substituents of the desirable substituent to the benzene ring is 1-3 in low-grade alkyl groups of carbon numbers 1-3, such as a methyl group, an ethyl group, i-propyl group, and n-propyl group. Especially desirable benzenesulfonic acid is p-toluenesulfonic acid. Moreover, these benzenesulfonic acid may be sodium salt or potassium salt. The addition of these benzenesulfonic acid is 0.02-3 mols per 1l. of developer constituents, and is 0.1-1 mol still more preferably 0.05-2 mols preferably.

[0041] The stability of the developer constituent of this invention improves further by in addition to this

adding a hydroxylamine derivative and surfactants of a certain kind.

[0042] The color development agent constituent of this invention is the gestalt, i.e., 1 so-called agent configuration, which included all the components contained in a used solution in one constituent. For it not being desirable to contact constituents generally for a long period of time etc., a constituent is divided into two or more liquids and solutions, and it considers as 2 agents or the developer constituent of 3 agent configurations in many cases (it is usually an international standard according to the name of ISO 5989, it is called 1, 2, 3 PERT configurations, etc.). Technical difficulty is also high although considering as a single part configuration has high practical use value because of the simple nature on an activity. This invention solves this and, moreover, realizes a high-concentration developer constituent with a single part configuration.

[0043] Although the developer constituent of a single part configuration is diluted with water and used as a development replenisher or a developer, about pH, only by diluting with water, the target pH is not acquired, but it may amend or adjust pH by addition of alkali chemicals (or acid). Unless the alkali (acid) agent is constituted as another parts also in this case, it is called the single part configuration.

[0044] Next, the container of the thick liquid development agent of this invention is explained further. The polyolefin resin used for the container of a thick liquid development agent constituent Polyethylene resin is desirable. To the polyethylene resin The pigment which does not carry out an adverse effect to alkaline development constituents, such as carbon black, a titanium white and calcium silicate, and a silica, Additives, such as calcium-carbonate, 2, and 6-G t-butyl-4-methyl phenol (BHT), JISECHIRU sulfide, a tris (laurylthio) FOSU fight, other amine systems, Skid agents, such as known antioxidants, such as a thioether system and a phenol system, stearin acid, or its metal salt, The known ultraviolet ray absorbent which has compatibility in polyethylene including a 2-hide ROKISHI-4-n-octyloxy benzophenone, the known plasticizer which has compatibility in polyethylene may be added as occasion demands. As for the total amount of these additives, it is desirable that it is 50% or less of the total amount of plastics raw material admixture. That in which the ratio of polyethylene does not contain a plasticizer at 85% or more preferably is good, and that in which the ratio of polyethylene does not contain a plasticizer at 95% or more more preferably good.

[0045] Shaping of a plastics bottle has shaping methods, such as injection molding, hollow (blow) shaping, injection entrainment shaping, after [ injection ] blow molding, extrusion molding, and a vacuum forming, and can adopt the shaping method according to the object. Most generally blow molding is used. In many cases, a cap is performed by injection molding and a bottle is performed for the bottle concerning this invention by blow molding or the blow molding after injection.

[0046] In this invention, while raising the airtightness of the checking-and-verifying section of a bottle and its cap, in order to give the buffer nature to an external impact, the construction material of a cap is also good to select a suitable thing. In addition, when calling it "a cap" in this invention, it is expressing it as the cap including the seal member of opening of a bottle. When using the ingredient which contains high density polyethylene (HDPE) 95% or more for the body of a bottle as a desirable mode of this invention, it is desirable to use for the cap of a bottle the ingredient which contains low density polyethylene (LDPE) 95% or more. Or even if it has made high density polyethylene (HDPE) into the subject for the cap, the confidentiality between a bottle and a cap can be raised to the construction material (for example, packing etc.) of the part which touches the body of a bottle by using the ingredient which contains low density polyethylene (LDPE) 95% or more. The consistencies of LDPE desirable as a cap and a sealing material are 0.91-0.94. To HDPE of the body of a bottle, the activities of little LDPE of this level to a cap or a seal are few, and do not bar the playback activity of plastics.

[0047] Although the configuration and structure of a container which are filled up with the thick liquid development agent constituent of this invention can be designed to arbitration according to the object, they can also use a thing with the flexible septum of a publication for an elastic mold given in JP,58-97046,A, 63-50839, JP,1-235950,A, JP,63-45555,A, etc., JP,58-52065,A, 62-246061, 62-134626, etc. at everything but general fixed form bottle structure.

[0048] Although it is good to be filled up so that up space may be made into the minimum as it fills [ whether it can do and ] to the month of a container, or the nitrogen purge of the up space may be

carried out and contact into the oxygen in air may be severed in order to face filling up a container with a developer constituent and to raise the safety to air oxidation further, this invention is not necessarily limited to such a restoration method.

[0049] In case the developer constituent of this invention is used with an auto-processor After equipping a developing machine with the container filled up with the developer constituent and pouring the constituent inside a container into a development supplement tub or a direct developer tank, the water used for washing while the water of a constant rate washed the inside of a container -- a supplement tub -- introducing -- preparation of a replenisher -- the development actuation method developed using the replenisher which used as service water, made such and was obtained is a method which uses the advantage of this invention effectively especially. Although washing of a spray method is desirable for the water of a constant rate especially washing the inside of a container, it is not necessarily limited to this. With this replenisher preparation method, wash water is used effectively and the quantity of the discharge of the waste water of a processing laboratory can be decreased. And it dissolved in the homogeneity which does not produce a sludge in the stability of this invention, it is thick, and since the developer constituent which miniaturized the volume can be designed so that contents may tend to flow out and rinsing of the container after it can also be managed with little water, it is suitable as a development agent equipped with the container soaping-machine style for automatic development radicals.

[0050] Therefore, it is simple by inclusion of the developer constituent especially described above as an advantageous embodiment of this invention, and the safety on an environment and an activity is also a large development system. For example, after using an auto-processor, equipping a developing machine with the container filled up with the development developer constituent of this invention and moving the contents into a development supplement tub, the chemical component which carried out spray washing of the interior of a container, and has adhered to the container wall is flushed, and the water used for washing can perform the development of silver halide color sensitive material by the approach of using it for preparation of a replenisher etc. In this case, if an auto-processor is loaded with the container of a developer constituent, the lid of a container will be unstopped automatically and it will have the structure by which fluid contents are discharged smoothly. Moreover, by the approach indicated by JP,6-82988,A, JP,8-220722,A, etc., the interior of a container becomes clarification, without applying a help with the spray of wash water, can be treated cleanly and becomes easy [ recycle of a waste container ]. And since wash water is used as some dissolution water of a developer, it does not serve as waste fluid. the small capacity condensed by the altitude with which the design for such a system was embodied by this invention -- moreover -- handling -- it is will not be realizable without the above-mentioned developer constituent with which easy sufficient fluidity is maintained over the long period of time. The example of the combination system of such a developer and a developer is explained in more detail later.

[0051] Next, the constituent of the developer constituent of this inventions other than the factor concerning the requirements for a configuration and the especially desirable mode of this invention described previously is explained directly. A developer constituent is the liquid of the alkaline continuous phase which contained the constituent contained in the usual color development agent in the state of the dissolution. Although a color development chief remedy is contained in it, in this invention, a 4-amino-3-methyl-N-ethyl-N-(beta-methane sulfo amide ethyl) aniline or its salt is used as the color development chief remedy which becomes main at least. This chief remedy is usually the form of salts, such as a sulfate, a hydrochloride, a sulfite, a naphthalene disulfon acid, and p-toluenesulfonic acid, in the state of a solid-state raw material. However, still a small amount of 4-amino-3-methyl-N-ethyl-N-(beta-hydroxyethyl) aniline or its salt may be added as an auxiliary color development chief remedy to the above-mentioned developing agent according to need, such as speeding up of a development. Moreover, in monochrome sensitive material, it adds in recent years so that a coupler may be colored black, and although there are some which form monochrome image using general-purpose common color development liquid, the developer constituent of this invention is applied also to processing of this kind of sensitive material.

[0052] although it is mixed with water (there is also a thing of the wash water of a container) by the ratio defined on the occasion of the activity and being used by using a processing agent constituent as the used solution of the form of a development replenisher (or developer diluted further) -- the concentration of this aromatic series primary amine developing agent in a used solution -- per 1l. of developers -- desirable -- 2 millimols - 200 millimol -- more -- desirable -- 12 millimol - 200 millimol, it dilutes so that it may become 12 millimols - 150 millimol still more preferably.

[0053] The processing agent constituent of this invention may contain little sulfite ion according to the class of target sensitive material, or may not contain it substantially. While sulfite ion has a remarkable stabilize action, it is also for being certain to have effect which is not desirable on the photograph-engine performance in a color development process depending on object sensitive material. In this invention, a hydroxylamine derivative or that of the \*\*\*\*\* is desirable. The alkyl hydroxylamine and carboxyl group in which a desirable hydroxylamine derivative has 1-8 alkyl groups of 2-4 carbon numbers, By being an alkyl hydroxylamine containing 1-2 alkyl groups of 2-4 carbon numbers permuted with a sulfonic group, a phosphono radical, and hydroxyl, and containing these The allowance width of face which it is possible to raise preservation stability furthermore and can extend the tolerance of the air transmission rate of a container by it, therefore makes thickness of a container thin or enlarges a specific surface increases. Moreover, the hydroxylamine derivative indicated by JP,1-97953,A, 1-186939, 1-186940, the 1-187557 official report, etc. may be further added in addition to the aforementioned hydroxylamine derivative.

[0054] The developer constituent of this invention may contain inorganic preservatives other than above-mentioned sulfite ion and an above-mentioned hydroxylamine derivative, and organic preservatives. Organic preservatives are making it contain to the processing liquid of sensitive material, and have pointed out the organic compound at large which reduces the degradation rate of an aromatic series primary-amine color developing agent. That is, although it is the organic compounds which have the function to prevent air oxidation of a color developing agent etc., the hydroxylamine derivative except said, hydroxamic acid, hydrazides, phenols, alpha-hydroxyketones, alpha-amino ketones, a saccharide, monoamines, diamines, polyamine, quarternary ammonium salt, nit ROKISHI radicals, alcohols, oximes, diamide compounds, condensed ring type amines, etc. are especially effective organic preservatives especially. these -- JP,63-4235,A, 63-30845, 63-21647, 63-44655, 63-53551, 63-43140, 63-56654, 63-58346, 63-43138, 63-146041, 63-44657, 63-44656, and U.S. Pat. No. 3,615,503 -- said -- 2,494,903 It is indicated by each official report or descriptions, such as a number, JP,52-143020,A, and JP,48-30496,B.

[0055] In addition, as preservatives, the aromatic series polyhydroxy compound of a publication etc. may be contained if needed on JP,57-44148,A and various metals given in a 57-53749 official report, salicylic acids given in JP,59-180588,A, the alkanolamines of the above mentioned general formula [A] and alkanolamines given in JP,54-3532,A, polyethyleneimine given in JP,56-94349,A, U.S. Pat. No. 3,746,544 descriptions, etc. Moreover, the alkanolamines like [ other than the above (for example, triethanolamine) ] may be added. As other amines, annular amines which were indicated by JP,63-239447,A, amines which were indicated by JP,63-128340,A, and amines which were indicated by JP,1-186939,A and the 1-187557 official report in addition to this can also be contained.

[0056] To the developer constituent of this invention, a chloride ion may be added if needed. As for a color developer (especially developer for color-print ingredients), although  $3.5 \times 10^{-2}$  to  $1.5 \times 10^{-1}$  mol / of chloride ions is usually contained 1. in many cases, since a chloride ion is usually emitted to a developer as a by-product of development, a replenisher has many things of addition needlessness. It is among a replenisher, therefore the amount of chloride ions in the processing agent constituent which becomes the basis is set up so that it may be set to the concentration level which the chlorine ion concentration in the developer tank when reaching running equilibrium composition described above. Chlorine ion concentration If [ than 1. ] more [ mol //  $1.5 \times 10^{-1}$  ], since it will have the fault of delaying development and quick nature and coloring concentration will be spoiled, it is not desirable. Moreover, in many cases, it is not desirable when preventing fogging by 1. in less than  $3.5 \times 10^{-2}$  two mols /.

[0057] About a developer constituent, it is in the same situation as the case of a chloride ion also about content of bromine ion. As for the bromine ion in a color developer, in processing of the charge of photography lumber, it is desirable that it is 1.0xten - three mols/l. or less in processing of about one to 5xten - three mols [ l. ] /and a print ingredient. Bromine ion may be added into a processing agent constituent if needed so that bromine ion concentration may become this range. When making it contain in a developer constituent, although sodium chloride, potassium chloride, ammonium-chloride, lithium-chloride, nickel chloride, magnesium chloride, manganese chloride, and calcium chloride \*\* is mentioned, desirable things are a sodium chloride and potassium chloride as chloride-ion feed materials. as the feed materials of bromine ion -- a sodium bromide, a potassium bromide, an ammonium bromide, a lithium bromide, a calcium bromide, a magnesium bromide, and bromination -- manganese, nickel bromide, and bromination -- a cerium and bromination -- although a thallium is mentioned, desirable things are a potassium bromide and a sodium bromide.

[0058] Since it is an important image quality property that the white ground of the background of a screen is white when the sensitive material by which a development is carried out is color photographic paper, it is important to finish white on appearance with a fluorescent brightener. Although a fluorescent brightener is included in sensitive material with the property, it may be made to permeate into sensitive material from processing liquid in the case of a development. In that case, according to the property of a fluorescent brightener, the suitable processing liquid for addition is chosen so that the high brightening effectiveness may be acquired. Therefore, it may be added by color development liquid with high pH. Generally a stilbene system fluorescent brightener is used abundantly, and the fluorescent brightener of a JI (triazyl amino) stilbene system, and the 4 and 4'-diamino -2 and a 2'-disulfo stilbene system is desirable also in it. Although especially desirable stilbene system fluorescent brighteners are the 4 and 4'-JITORI azinyl amino -2 and a 2'-disulfo stilbene, this invention is not limited to these.

[0059] The stilbene system fluorescent brightener used can be well-known, and can come to hand easily, or can be easily compounded by the well-known approach. This stilbene system fluorescent brightener can be added to either desilvering liquid besides color development liquid, or sensitive material. When making it contain in color development liquid, the suitable concentration is 1x10-4 to 5xten - two mols/l., and is 2x10-4 to 1xten - two mols/l. more preferably. An addition is decided that, as for the processing agent constituent of this invention, the development of a busy condition contains a fluorescent brightener on this concentration level.

[0060] In order that pH of the developer constituent of this invention may make high concentration contain a color development chief remedy, pH is set up highly, is usually in the range of 11.0-13.5, and is in the range of 12.0-13.5 preferably, and the range of it is 12.5-13.5 more preferably. And the color developer prepared and a development replenisher are more preferably used by 10.0-12.5 9.5 or more pH. In order to hold pH to stability, it is desirable to use various buffers. As a buffer, a carbonate, phosphate, a borate, tetraborate, a hydroxybenzoic-acid salt, a glycyl salt, a N,N-dimethylglycine salt, a leucine salt, a norleucine salt, a guanine salt, a 3, 4-dihydroxyphenylalanine salt, an alanine salt, an aminobutyric acid salt, the 2-amino-2-methyl -1, 3-propanediol salt, a valine salt, a proline salt, a tris hydroxy aminomethane salt, a lysine salt, etc. can be used. As for especially a carbonate, phosphate, tetraborate, and a hydroxybenzoic-acid salt, it is desirable to excel in the buffer capacity in a with a pH of 9.0 or more high pH field, for there to be no adverse effects (fogging etc.) to a photograph engine-performance side, even if it adds to a color developer, to have the advantage of being cheap, and to use these buffers so that the range of the specific gravity of this invention may be suited.

[0061] As an example of these buffers, a sodium carbonate, potassium carbonate, Sodium bicarbonate, potassium bicarbonate, phosphoric-acid 3 sodium, phosphoric-acid 3 potassium, Phosphoric-acid disodium, phosphoric-acid 2 potassium, the sodium borate, a boric-acid potassium, Sodium tetraborate (borax), a tetraboric-acid potassium, o-hydroxybenzoic acid sodium (sodium salicylate), An o-hydroxybenzoic acid potassium, 5-sulfo-2-hydroxybenzoic-acid sodium (5-sulfosalicylic acid sodium), a 5-sulfo-2-hydroxybenzoic-acid potassium (5-sulfosalicylic acid potassium), etc. can be mentioned. However, this invention is not limited to these compounds. Especially a desirable buffer has the advantage that it is possible to increase specific gravity effectively to especially desirable potassium

carbonate, without depositing, since solubility is high. the concentration in the color development replenisher in which the amount of this buffer carried out dilution preparation -- 0.01-2 mols/l. or more -- especially -- It is added in a constituent so that it may become in l. and 0.1 mols/l. - 0.5 mols /.

[0062] In the developer constituent of this invention, the various chelating agents which are suspending agents of other color developer components, for example, calcium, and magnesium, or are also stability improvers of a color developer can also be added. For example, nitrilotriacetic acid, a diethylenetriamine pentaacetic acid, ethylenediaminetetraacetic acid, N, N, and N-trimethylene phosphonic acid, ethylenediamine - N, N, N', and N'-tetramethylene sulfonic acid, Ethylenediamine N, N-JI succinic acid, N, and N-JI (carboxylate)-L-aspartic acid, beta-ARANINJI succinic acid, 2-phosphono butane - 1, 2, 4-tricarboxylic acid, A 1-hydroxy ethylidene -1, 1-diphosphonic acid, N, N'-screw (2-hydroxybenzyl) ethylenediamine-N, and N'-JI acetic acid, 1, 2-dihydroxybenzene -4, 6-disulfonic acid, etc. are mentioned. Two or more sorts of these chelating agents may be used together if needed. The amount of these chelating agents is per l. that what is necessary is just sufficient amount to block the metal ion in a color developer. It adds so that it may become about 0.1g-10g.

[0063] The developer constituent of this invention can add the accelerator of arbitration as occasion demands. As an accelerator, JP,37-16088,B, 37-5987, The thioether system compound expressed with each official report or descriptions, such as 38-7826, 44-12380, 45-9019, and U.S. Pat. No. 3,813,247, The p-phenylene diamine system compound expressed by JP,52-49829,A and the 50-15554 official report, The quarternary ammonium salt expressed by JP,50-137726,A, JP,44-30074,B, JP,56-156826,A, the 52-43429 official report, etc. U.S. Pat. No. 2,494,903 -- said -- 3,128,182 a number -- said -- 4,230,796 a number -- said -- 3,253,919 a number, JP,41-11431,B, and U.S. Pat. No. 2,482,546 -- said -- 2,596,926 a number -- and -- said -- 3,582,346 an amine system compound given in each official report or descriptions, such as a number, -- JP,37-16088,B, 42-25201, U.S. Pat. No. 3,128,183, The polyalkylene oxide expressed with each official report or descriptions, such as JP,41-11431,B, 42-23883, and U.S. Pat. No. 3,532,501, other 1-phenyl-3-pyrazolidone, imidazole derivatives, etc. can be added if needed.

[0064] The developer constituent of this invention can add the fogging inhibitor of arbitration if needed. As a fogging inhibitor, the alkali-metal halogenide and the organic fogging inhibitor like a sodium chloride, a potassium bromide, and a potassium iodide can be used. As an organic fogging inhibitor, the nitrogen-containing heterocycle compound like benzotriazol, 6-nitrobenzimidazole, 5-nitroglycerine iso indazole, 5-methyl benzotriazol, 5-nitrobenzo triazole, 5-chloro-benzotriazol, 2-thiazolyl-benzimidazole 2-thiazolyl methyl-benzimidazole indazole, hydroxyazaindolizine, and an adenine can be raised as an example of representation, for example. Moreover, various surfactants, such as an alkyl sulfonic acid, an aryl sulfonic acid, aliphatic carboxylic acid, and aromatic carboxylic acid, may be added if needed in addition to the above mentioned surfactant. The color development replenisher or developer prepared from the color development constituent of this invention and it was explained above.

[0065] When the sensitive material by which a development is carried out is a color-print ingredient, the processing temperature of the color development applied to this invention is 30-55 degrees C, is 35-55 degrees C preferably, and is 38-45 degrees C more preferably. Development time amount is 5 - 90 seconds, and is 15 - 60 seconds preferably. Although little direction of the amount of supplements is desirable, 15-600ml per two is [ 1m of sensitive material ] suitable, and 15-120ml is 30-60ml especially preferably preferably. On the other hand, in color development processing of the Calah-negative and a color reversal film, development temperature is 20-55, and it is 30-55 degrees C preferably, and it is 38-45 degrees C more preferably. Development time amount is 20 seconds - 6 minutes, and, in the case of a color negative, is 30 - 200 seconds preferably. Moreover, in the Calah-reversal, 2 - 6 minutes is especially desirable. Although little direction of the amount of supplements is desirable, 100-1200ml per two is [ 1m of sensitive material ] suitable, and 200-500ml is 250-400ml especially preferably preferably.

[0066] In operation of this invention, it goes into desilvering down stream processing following a development process with the color development liquid prepared using the development agent constituent of this invention, and processing by bleach liquor and the bleach fix bath is made. A stilbene

system fluorescent brightener is contained preferably a compound with the fluorescent brightener suitable in processing of the sensitive material for a color-print described above also in this processing liquid, and often. Although a well-known bleaching agent can also be used as a bleaching agent used in bleach liquor or a bleach fix bath, it is especially iron (III). Organic acids, such as organic complex salt (for example, complex salt of amino polycarboxylic acid) or a citric acid, a tartaric acid, and a malic acid, persulfate, a hydrogen peroxide, etc. are desirable.

[0067] It is iron (III) among these. Especially organic complex salt is desirable from a viewpoint of quick processing and environmental pollution prevention. Iron (III) Ethylene JIAMINJI succinic acid (SS object), N which have biodegradability when useful amino polycarboxylic acid or those salts are enumerated, in order to form organic complex salt -(2-carboxylate ethyl)- Ethylenediaminetetraacetic acid, a diethylenetriamine pentaacetic acid, 1, 3-diaminopropane tetraacetic acid, a propylenediamine tetraacetic acid, nitrilotriacetic acid, cyclohexanediaminetetraacetic acid, an iminodiacetic acid, glycol ether diamine tetraacetic acids including L-asparatic acid, beta-alanine diacetic acid, and methyl iminodiacetate, etc. can be mentioned. Any of sodium, a potassium, CHIRIUMU, or ammonium salt are sufficient as these compounds. In these compounds, they are ethylene JIAMINJI succinic acid (SS object) and N. -(2-carboxylate ethyl)- L-asparatic acid, beta-alanine diacetic acid, ethylenediaminetetraacetic acid, 1, 3-diaminopropane tetraacetic acid, and methylimino 2 acetic acid are the iron (III). Complex salt is desirable from the good thing of photograph nature. Such 2nd iron ion complex salt may be used in the form of complex salt, and the 2nd iron ion complex salt may be made to form in a solution using the 2nd iron salt, for example, ferric sulfate, ferric chloride, ferric nitrate, ferric ammonium sulfate, the 2nd iron of phosphoric acid, etc. and chelating agents, such as amino polycarboxylic acid. Moreover, a chelating agent may be superfluously used, more than it forms the 2nd iron ion complex salt. These iron (III) 0.01-1.0 mols /of 0.05-0.50 mols /of additions of an organic complex are [ 1. / 1. ] 0.10-0.50 mols/l. still more preferably in a replenisher, and a bleaching agent constituent is designed so that it may become the replenisher of this concentration by dilution.

[0068] Bleaching time amount is usually 1 minute from 10 seconds in the desirable bleaching processing 30 seconds - 4 minutes and 30 seconds, and for color-print ingredients for 0 second to 1 6 minutes and 30 seconds.

[0069] water-soluble silver halide resolvents, such as thioether compounds, such as thiocyanates, such as thiosulfates, such as a fixing agent with the well-known fixing agent used for a bleach fix bath or a fixer, i.e., a sodium thiosulfate, and ammonium thiosulfate, a sodium thiocyanate, and ammonium thiocyanate, ethylene bis-thioglycolic acid, 3, 6-dithia -1, and 8-octanediol, and thiourea, -- it is -- these -- one sort -- or two or more sorts can use it, mixing. Moreover, the special bleach fix bath which consists of combination of the halogenide like the fixing agent indicated by JP,55-155354,A and a lot of potassium iodides etc. can be used. In this invention, the activity of a thiosulfate, especially an ammonium thiosulfate salt is desirable. 0.3-2 mols are desirable still more desirable, and the range of the amount of the fixing agent per l. is 0.5-1.0 mols.

[0070] As for pH field of the bleach fix bath concerning this invention, or a fixer, 3-8 are desirable, and also 4-especially 7 are desirable. Although desilvering nature will improve if pH is lower than this, degradation of liquid and leuco \*\* of cyanogen coloring matter are promoted. Conversely, if pH is higher than this, desilvering will become easy to generate delay and a stain. It is eight or less, as for pH field of the bleach liquor used for this invention, 2-7 are desirable, and 2-especially 6 are desirable. If pH is lower than this, degradation of liquid and leuco \*\* of cyanogen coloring matter will be promoted, and if pH is conversely higher than this, desilvering will become easy to generate delay and a stain. In order to adjust pH, a hydrochloric acid, a sulfuric acid, a nitric acid, a bicarbonate, ammonia, caustic potash, caustic alkali of sodium, a sodium carbonate, potassium carbonate, etc. can be added if needed.

[0071] Moreover, in addition to this, a bleach fix bath can be made to contain organic solvents, such as various kinds of fluorescent brighteners, a defoaming agent or a surface active agent, a polyvinyl pyrrolidone, and a methanol. As for a bleach fix bath or a fixer, it is desirable to contain ant-RUSURU fin acids, such as sulfite ion bleedoff compounds, such as sulfites (for example, a sodium sulfite, potassium sulfite, ammonium sulfite, etc.), bisulfites (for example, heavy ammonium sulfite, sodium

bisulfite, potassium bisulfite, etc.), and metabisulfite (for example, potassium metabisulfite, sodium metabisulfite, meta-pile ammonium sulfite, etc.), and p-toluene sulfenic acid, m-carboxy benzenesulfenic acid, etc. as preservatives. It converts into sulfite ion or sulfenic-acid ion, and these compounds are about 0.02-1.0. It is desirable to carry out a mol / liter content.

[0072] As preservatives, others, an ascorbic acid, a carbonyl pile sulfurous-acid addition product or a carbonyl compound, etc. may be added. [ above ] Furthermore, a buffer, a fluorescent brightener, a chelating agent, a defoaming agent, an antifungal agent, etc. may be added if needed. the bleaching fixation processing in connection with this invention -- the processing time -- it is 10 - 60 seconds preferably for 5 to 240 seconds. 25 degrees C - 60 degrees C of processing temperature are 30 degrees C - 50 degrees C preferably. Moreover, 20ml - the 250ml per sensitive material one m<sup>2</sup> of 30ml - the 100ml of the amounts of supplements is 15ml - 60ml especially preferably preferably.

[0073] It is common after desilvering processing of fixation or bleaching fixation to carry out rinsing and/or stabilizing treatment. rinsing at a rinsing process -- amount of water can be broadly set up according to the number (number of stages) of the property (for example, based on activity raw materials, such as a coupler) of sensitive material, an application and rinsing water temperature, and rinsing tanks, and other various conditions. Among these, the number of rinsing tanks in a multistage counterflow method and the relation of amount of water are journal and OBU THE society OBU motion picture - and - tele vision en JINIAZU. (Journal of the Society of Motion Pictureand Television Engineers) It is the approach of a publication and the 64th volume and p.248-253 (1955 the year May issue) can be asked. Usually, as for the number of stages in a multistage counterflow method, 3-15 are desirable, and especially 3-10 are desirable.

[0074] according to a multistage counterflow method -- rinsing -- the problem of being able to decrease sharply and the suspended matter which bacteria bred by the increment in the residence time of the water within a tank, and was generated adhering to sensitive material produces amount of water. The approach of making JP,62-288838,A reducing the calcium of a publication and magnesium as a solution of such a problem can be used very effectively. Moreover, the germicide of a publication can also be used for the volume chlorine-based germicides, such as an iso thiazolone compound given in JP,57-8542,A, and chlorinated-isocyanuric-acid sodium given in sire vendor ZORU and a 61-120145 official report, benzotriazol given in JP,61-267761,A, a copper ion, other Horiguchi \*\*\*\* "chemistry of antimicrobic mildewproofing" (1986) Sankyo Publishing, and on health technical meeting, a "sterilization [ of a microorganism ], sterilization, and mildewproofing technical" (1982) technology meeting, and the edited by Society for Antibacterial and Antifungal Agents, Japan "an antifungal agent encyclopedia" (1986).

[0075] Furthermore, a surfactant and the chelating agent represented by EDTA as a water softener can be used for rinsing water as a ridge agent. It can also process by direct slurry, without passing through a rinsing process following the above rinsing process. The aldehyde compound which the compound which has an image stabilization function is added, for example, is represented by formalin, the buffer for preparing on the film pH suitable for coloring matter stabilization, and an ammonium compound are raised to slurry. Moreover, the azo RIRUME chill amines of a publication etc. are added by aldehydes, such as formaldehyde which inactivates the Magenta coupler which remains and prevents the tenebrescence of coloring matter, and generation of a stain, an acetaldehyde, and pyruvic aldehyde, a methylol compound given in U.S. Pat. No. 4786583 and a hexamethylenetetramine, hexahydrotriazine given in JP,2-153348,A, a formaldehyde pile sulfurous-acid addition product given in U.S. Pat. No. 4921779, the seizure patent disclosure official report No. 504609, said 519190 numbers, etc. Moreover, since fungus resistance is given to the sensitive material after propagation prevention of the bacteria in the inside of liquid, or processing, the various above mentioned germicides and the above mentioned antifungal agent can be used.

[0076] Furthermore, a surfactant, a fluorescent brightener, and a hardening agent can also be added. In the processing concerning this invention, when carried out directly, without stabilization passing through a rinsing process, all the well-known approaches of a publication can be used for JP,57-8543,A, 58-14834, a 60-220345 official report, etc. In addition, it is also a desirable mode to use chelating

agents, such as the 1-hydroxy ethylidene -1, 1-diphosphonic acid, and ethylenediamine 4 methylene phosphonic acid, magnesium, and a bismuth compound.

[0077] The so-called rinse is similarly used as the wash bath or stabilizer used after desilvering processing. Desirable pH of a rinsing process or a stabilization process is 4-10, and is 5-8 still more preferably. Although temperature can be variously set up in the application, the property, etc. of sensitive material, generally 20 degrees C - 50 degrees C are 25 degrees C - 45 degrees C preferably. Desiccation is performed following rinsing and/or a stabilization process. After coming out from a viewpoint which reduces the amount of carrying in of the moisture to the image film from a wash bath, it is also possible to bring desiccation forward by absorbing water with a squeeze roller, cloth, etc. immediately. Although it is natural as an improvement means from a dryer side, it is possible to bring desiccation forward by changing the configuration of to make temperature high or a spray nozzle, and strengthening a desiccation wind etc. Furthermore, desiccation can be brought forward also by adjustment of the air blasting include angle to the sensitive material of the desiccation style, and the clearance approach of the blowdown style as indicated by JP,3-157650,A.

[0078] The good development system of the workability in which water is not especially impressed as an advantageous embodiment combining processing equipment can consist of that it is the simple configuration of [ it is compact and ] a single part configuration many cases which the color development material constituent of this invention thickened. Although the development system which equips with the bottle of the development supplement agent constituent of this invention as the example, carries out automatic unstopping, and performs automatic mixing of a replenisher to below is explained, application of this invention is not limited to this. The outline of the printer processor 10 in which this invention was applied is shown in drawing 1 , and the perspective view of the printer processor 10 is shown in drawing 2 . The photograph printing section 12 which constitutes the printer section of this printer processor 10 has the structure where it can load with the paper magazine 14 with which photographic paper P was contained.

[0079] The driving roller 16 around which near the point of photographic paper P is wound almost is supported free [ a revolution ] at the drawing 1 top of this paper magazine 14, and the upper left side, since the carrier roller 18 of a couple is arranged through photographic paper P, a driving roller 16 will pinch photographic paper P in the location which countered the driving roller 16 among these carrier rollers 18, and photographic paper P will be sent out to it into the photograph printing section 12.

[0080] Moreover, after the beam of light irradiated from the light source 26 which is outside casing 10A which constitutes the outer frame of the printer processor 10, and is arranged right above [ of easel equipment 64 ] passes CC filter 24, It is crooked being spread with the diffusion box 28, and is sent to directly under, and this beam of light penetrates the negative film N on NEGAKYARIA 30. The beam of light which furthermore penetrated the negative film N and turned into an image Mr. beam of light (image support light) carries out image formation of the image of a negative film N on the photographic paper P which passes the zoom lens 38 which can change prism 36 and magnifying power, and is located under easel equipment 64.

[0081] The photographic paper P sent out from the paper magazine 14 in the photograph printing section 12 be cut by the cutter 22 , the cut photographic paper P be conveyed with the endless belt 44 in the image printing location which be a location on the optical axis line S of the exposure beam of light of the lower part of the easel equipment 64 on susceptor 46 , and printing exposure of the image with which the black shutter 41 be recorded on the negative film N by predetermined time open Lycium chinense be carried out on photographic paper P .

[0082] Furthermore, it is pinched between a guide roller 56 and the presser-foot roller 58, the conveyance direction is changed perpendicularly horizontally, and the photographic paper P which printing exposure of an image ended is sent out perpendicularly. Then, as shown by the path K showing the conveyance path of photographic paper P, photographic paper P is conveyed to the processor section 72 which performs each processing of development, bleaching, fixation, rinsing, and desiccation through the conveyance way 60 constituted with two or more pairs of rollers.

[0083] The developer is accumulated in the developer tank 74 of the processor sections 72, photographic

paper P is dipped in this developer, and a development is performed. The photographic paper P by which the development was carried out is conveyed to the bleaching fixation tub 76 which adjoins a developer tank 74. The bleach fix bath is accumulated in the bleaching fixation tub 76, photographic paper P is dipped in this bleach liquor, and bleaching processing is performed. The photographic paper P by which bleaching fixation processing was carried out is conveyed to the rinse tank 79 which adjoins the bleaching fixation tub 76. Rinsing water is filled in two or more rinse tanks 79, respectively, photographic paper P is dipped in the rinsing water in a rinse tank, and rinsing processing is performed. [0084] The photographic paper P by which rinsing processing was carried out is conveyed to the dryer part 80 located in the upper part of a rinse tank 79. A dryer part 80 exposes photographic paper P to the hot blast ventilated along the direction of arrow-head B from the chamber 82 side arranged at the conveyance path bottom of photographic paper P, and dries photographic paper P. The photographic paper P which desiccation processing was completed and was discharged from the dryer part 80 through the conveyance way 84 is discharged in the exterior of the printer processor 10, and is accumulated. [0085] Moreover, the supplement section is prepared in the processor section 72. It is, automatic unstopping of management of a processing agent kit and a processing agent kit, automatic washing, and desiccation are mainly carried out at the loading section 300, and the loading section 300 by which the supplement section is loaded with a processing agent kit (it mentions later), and the supplement tank part by which a replenisher is managed mainly carry out management of the oil-level level of a supplement tub (it mentions later), supplement pump actuation, and a circulation stirring pump (it mentions later) at a supplement tank part. Moreover, the sensor 73 for detecting the throughput of photographic paper P is formed in the inlet port of a developer tank 74.

[0086] In addition, to the above-mentioned developer tank 74 and the bleaching fixation tub 76, it is the system supplemented with a replenisher from the supplement tub installed in the processor section 72.

[0087] (Processing agent kit) With this operation gestalt, when the replenishers in a supplement tub run short, it is the system which sets to the loading section 300 (refer to drawing 2 ) which formed the processing agent kit 202 shown in drawing 3 in the up transverse-plane side of casing 10A, and pours in a processing agent (water solution condensed with this operation gestalt).

[0088] As shown in drawing 3 , the processing agent kit 202 of this operation gestalt has held the container 207 with which the fixation processing agent component of the container 203 with which the development agent was stored by the carton 204, the container 205 with which the bleaching processing agent component of a bleach fix bath was stored, and a bleach fix bath was stored.

[0089] In addition, since containers 203, 205, and 207 are the same structures respectively, they explain structure on behalf of a container 203 below. As shown in drawing 4 , the container 203 is equipped with the screw cap 208 which projects from a carton 204, and the flange 212 is formed in the screw cap 208. Opening of a container 203 is blockaded with the seal 210 of the resin film inserted between screw caps 208. Moreover, the hole 209 is formed in the center of a screw cap 208, and it is constituted so that a seal 210 may be pushed and it may be torn with the washing nozzle 346.

[0090] this operation gestalt -- 1300ml and a container 207 are filled up with the bleaching processing agent component of a bleach fix bath, and the container 203 is filled up with 1300ml of fixation processing agent components of a bleach fix bath for the development agent at 1300ml and a container 209.

[0091] It becomes the replenisher (5000ml as completion liquid) with which 3700ml of dilution waters is added to 1300ml, and a developer tank 74 is supplemented. moreover, a development agent -- It becomes the replenisher (2000ml as completion liquid) of the bleaching agent component with which 700ml of dilution waters is added to 1300ml, and the bleaching fixation tub 76 is supplemented. a bleaching processing agent -- It becomes the replenisher (2000ml as completion liquid) of the fixing agent component with which 700ml of dilution waters is added to 1300ml of fixation processing agent components, and the bleaching fixation tub 76 is supplemented.

[0092] (Loading section) As shown in drawing 2 and drawing 3 , the loading section 300 is covered with the loading section covering 302 which can be opened and closed. In addition, the condition of having shut the loading section covering 302 is in the condition shown in drawing 3 as a continuous line, and it

is in the condition that an open beam condition shows the loading section covering 302 to a fictitious outline (two-dot chain line) at drawing 3. The electrode holder 316 carrying the processing agent kit 202 is formed in the loading section 300.

[0093] If the washing nozzles 346, 348, and 350 are setting up in the location which corresponded to drawing 3 with opening of containers 203, 205, and 207 under the electrode holder 316 so that it might be shown and containers 203, 205, and 207 are caudad moved to it, the washing nozzle 346 will unstopp by the washing nozzle's 348 pushing the seal 210 of a container 205, and the washing nozzle's 350 pushing the seal 210 of a container 207, tearing the seal 210 of a container 203, and advancing into a container.

[0094] as shown in drawing 3, the funnel 352 which inserted the soffit in the developer supplement tub (the lower part of the funnel of the lower part of drawing 3 -- not shown) under the washing nozzle 346 is arranged, the funnel 354 which inserted the soffit in the bleaching agent component supplement tub of a bleach fix bath under the washing nozzle 348 is arranged, and the funnel 356 which inserted the soffit in the supplement tub of the fixing agent component of a bleach fix bath under the washing nozzle 350 is arranged.

[0095] (Configuration of a processing agent kit and its container) The configuration of the bottle 1300 as containers 203, 205, and 207 for photographic-processing agent kit 202 concerning the gestalt of 1 operation of this invention is explained below based on drawing 5.

[0096] The bottle 1300 is equipped with the body 1302 of a container as shown in drawing 5. The body 1302 of a container is formed in box-like [ in the air ] of resin material. Moreover, the upper bed section of the body 1302 of a container is made into the shape of a taper whose diameter was reduced gradually, and the cylinder-like neck 1306 with which the male screw 1304 was cut by the periphery section is formed. Opening of the upper bed section of this neck 1306 is carried out, and receipts and payments of the replenisher mentioned above through this opening can be performed. Moreover, the polyethylene sheet 1308 as a seal member is arranged at the upper bed section of a neck 1306. The gash of a cross-joint mold is minced and this polyethylene sheet 1308 is formed in the form which tends to be broken through by the \*\*\* nozzle.

[0097] Moreover, the bottle 1300 is equipped with the cap 1310 as a holddown member. It is formed in the shape of [ which carried out opening towards the neck 1306 ] a cylinder like object with base, among those the female screw 1318 corresponding to the male screw 1304 formed in the neck 1306 is cut by the periphery, and this cap 1310 can be screwed to a neck 1306, and by screwing to a neck, at the pars basilaris ossis occipitalis 1312 of cap 1310, the polyethylene sheet 1308 can be fixed to a presser foot, and it can fix the polyethylene sheet 1308 to a neck 1306. Moreover, the circular opening 1314 is formed in the pars basilaris ossis occipitalis 1312 of cap 1310, and where cap 1310 is inserted in, the polyethylene sheet 1308 can be punched.

[0098] (Operation of the gestalt of this operation) next, it attaches [ it is alike and ] and explains to an operation of the gestalt of this operation. For example, if the development of the photographic paper P is carried out within the developer tank 74 of drawing 1, a supplement pump will operate according to this, the development replenisher which was once able to be stored on the supplement tank 347 will be sent to a developer-tank 74 side, and the development replenisher of an amount which was used for processing within a developer tank 74, and deteriorated will be filled up. In addition, these are the same also in a bleach fix bath. If the oil level within a supplement tank becomes below the specified quantity, a float switch will detect this and directions of supply on the supplement tank of a replenisher will be displayed on the monitor 122 of drawing 2.

[0099] Next, the procedure at the time of supplementing the supplement tank 347 of drawing 1 with a replenisher is explained. First, opening the closing motion door 302 of the supplement section 300 of drawing 2, and inserting the neck (1306 of drawing 5) of a container 203 (bottle 1300 of drawing 5) in the hole 318 of the electrode holder 316 of drawing 3, a container 203 is pushed in and it lays on an electrode holder 216. If the control unit which does not shut and (continuous-line condition of drawing 3) illustrate the closing motion door 302 in this condition is operated, a motor drives, the punching nozzle 346 will move upwards and the seal 210 of the polyethylene prepared in the opening 209 of the

cap 208 of the container 203 of drawing 4 will be broken through. The liquid in a container 203 flows and falls by this.

[0100] Thus, the replenisher which flowed and fell from the container 203 of drawing 4 is fed into the supplement tank which is not illustrated. If the bottle 1300 of drawing 5 which starts the gestalt of this operation here is applied, an operator will open the closing motion door 302 of drawing 2, a bottle 1300 will be set, the closing motion door 302 will only be shut, and an opening activity and a supplement activity, i.e., the activity which punches the polyethylene sheet 1308 and supplements a supplement tank with a replenisher, will be done by the inside of the closed supplement section 300. It seems that for this reason, the troublesome activity that an operator has a bottle 1300 by hand and fills it up is not needed, but a replenisher moreover disperses in the case of a supplement, and an operator's hand or dress are not soiled.

[0101] Next, in the state of drawing 4, after the inside of the body 203 of a container flows thoroughly and falls, washing of a container and desiccation are performed. By washing, while switching the cross valve which operates first the control unit which is not illustrated and the above does not illustrate, the wash water conveying pump of the feed pipe section from the wash water flush tank which is not illustrated operates, and the wash water in a wash water flush tank is fed into the punching nozzle 346 with predetermined water pressure through a pipe. Thereby, wash water is injected from the stoma of the punching nozzle 346, and the interior of a container 203 is washed. The wash water after washing flows and falls from a container 203.

[0102] Subsequently, termination of washing of predetermined conditions (for example, predetermined time) suspends a wash water conveying pump. Furthermore, in this condition, the dryer part and fan who do not illustrate operate, a desiccation wind is guided to a fan from a dryer part, and a desiccation wind is further sent into the punching nozzle 346 through a pipe and a cross valve from a fan. Thereby, the interior of the blowdown and a container 203 is dried for a desiccation wind from the stoma of the punching nozzle 346.

[0103] After these washing and desiccation are completed, the container 203 which opened the closing motion door 302 and became empty is taken out, and it is exchanged for another new container, but from this condition, since the interior of the taken-out container is washed and it is moreover dry, in case it takes out, neither a hand nor dress becomes dirty with an excessive replenisher etc.

[0104] Furthermore, in the case of the bottle 1300 of drawing 5, although the taken-out empty container 203 is recycled, cap 1310 is removed from the neck 1306 of the body 1302 of a container, further, the polyethylene sheet 1308 and packing 1316 are removed and it is collected by type for every construction material. Here, the body 1302 of a container, cap 1310, the polyethylene sheet 1308, and packing 1316 are used as another soma article with which each became independent, and are stuck to the polyethylene sheet 1308 which attaches these through packing 1316 to the neck 1306 of the body 1302 of a container. Therefore, by removing cap 1310 from the body 1302 of a container, the polyethylene sheet 1308 and each part article of packing 1316 are removed easily, and it can dissociate. And since it does not tear and remain like [ in the case of having fixed the polyethylene sheet 1308 directly to the neck 1306 ] in case the polyethylene sheet 1308 is removed, activity manday is mitigable.

[0105] In addition, with the gestalt of this operation, although the bottle 1300 was made into the development replenisher for printer processor 10, the replenisher of the bleaching agent component of a bleach fix bath, and the replenisher of the fixing agent component of a bleach fix bath, you may use it for the liquid supplement of other development systems other than printer processor 10.

[0106] Moreover, with the gestalt of this operation, although it has the thickness which does not cause degradation of the processing agent constituent by transparency of air into the reserve time of a bottle, the polyethylene sheet 1308 with a cross gash as a seal member is formed so that a cross gash may be easily broken by the nozzle.

[0107] The color photography sensitive material which is the object for application of the development approach which uses the color development agent constituent of this invention is explained. The approach of this invention is applicable to a general color photography sensitive material regardless of the object for photography, and the object for a print. That is, it can apply to any development of a

negative color film, a color reversal film, and color photographic paper, and can apply to the object for the object for general, and films, and all for professional. The effectiveness of application to the development of the color photographic paper in which especially white whiteness is thought as important is large.

[0108] As for the photosensitive silver halide emulsion in the sensitive material as positive ingredients, such as a color paper, it is desirable to consist of a silver halide particle in which the remainder is a silver bromide at at least 95-mol %, and silver chloride content does not contain silver iodide substantially. "silver iodide not being included substantially" here -- silver iodide content -- less than [ 1 mol % ] -- desirable -- less than [ 0.2 mol % ] -- zero-mol % is meant still more preferably. Moreover, silver chloride content has [ especially the above-mentioned silver halide emulsion ] a desirable silver halide emulsion beyond 98 mol % from a viewpoint of quick processability. It is desirable especially from high sensitivity being obtained for what has a silver-bromide localization phase on the front face of a silver chloride particle, and moreover being able to attain stabilization of the photograph engine performance also in such a silver halide.

[0109] The silver halide photographic emulsion which can be used for this invention For example, research disclosure No.17643 (December, 1978), 22-23 pages, "I. emulsion manufacture (Emulsion preparation and types)", (It abbreviates to RD hereafter) and -- said -- No.18716 (November, 1979) and 648 pages -- said -- No.307105 (198911 moons) -- Physics of a photograph, and 863-865-page and "chemistry" pole MONTERU Co. \*\* written by Glafkides (P. Paul Montel [ Glafkides, Chemie et Phisique Photographique and J) 1967, the Duffin work "photographic-emulsion chemistry", the Focal Press Co. \*\* (G. F.Duffin, Photographic Emulsion Chemistry, Focal Press, 1966), The approach indicated by manufacture of a photographic emulsion, "spreading" Focal Press Co. \*\* written by ZERIGUMAN (V. L.Zelikman, et al., Making and Coating Photographic Emulsion, Focal Press, 1964), etc. It can use and prepare.

[0110] The raw material for photographs and additive of \*\*\*\* can be conventionally used for the silver halide photosensitive material set as the object of this invention. for the object of this invention, a reflective mold base material is desirable, and the reflective base material which it laminates in two or more polyethylene layers and polyester layers especially, and such a waterproof resin layer (lamination layer) is further alike at least, and contains white pigments, such as titanium oxide, is desirable for it.

[0111] Furthermore, it is desirable to contain a fluorescent brightener in the aforementioned waterproof resin layer. Moreover, a fluorescent brightener may be distributed in the hydrophilic colloid layer of a sensitized material. As a fluorescent brightener, preferably, a benzo oxazole system, a coumarin system, and a pyrazoline system can use, and it is the fluorescent brightener of a benzoxazolyl naphthalene system and a benzoxazolyl stilbene system still more preferably. Although especially the amount used is not limited, it is 1 - 100 mg/m<sup>2</sup> preferably. The mixing ratio in the case of mixing to waterproof resin is 0.0005 - 3 % of the weight to resin preferably, and is 0.001 - 0.5 % of the weight still more preferably. What painted the hydrophilic colloid layer containing white pigments on the body may be used.

Moreover, a reflective mold base material may be a base material with the surface of metal of specular reflection nature or the 2nd sort diffuse reflection nature. In the sensitive material concerning this invention, in order to raise the sharpness of an image etc. in a hydrophilic colloid layer Europe patent EP 0,337,490A2 To the 27-76th page of a number description, a publication, So that optical reflection density [ in / for the color (even inside oxo-Norian system color) which can be decolorized by processing / 680nm of this sensitive material ] may become 0.70 or more add or It is desirable to carry out content of the titanium oxide by which surface preparation was carried out with the alcohols (for example, trimethylolethane) of 2 - tetravalence etc. into the waterproof resin layer of a base material 12% of the weight or more (preferably 14 % of the weight or more).

[0112] Moreover, in order to prevent various kinds of mold and bacteria which it breeds [ bacteria ] in a hydrophilic colloid layer and degrade an image in the sensitive material concerning this invention, it is desirable to add an antifungal agent like a publication to JP,63-271247,A.

[0113] Even if the sensitive material concerning this invention is exposed by the light, it may be exposed by infrared light. As the exposure approach, low illuminance exposure or high illuminance

short-time exposure is sufficient, and, especially in the case of the latter, a laser scan exposure method with the exposure time shorter than 10 to 4 seconds per pixel is desirable.

[0114] As the approach applied in order to process this sensitive material in the silver halide emulsion applied to the sensitive material concerning this invention, other raw materials (additive etc.) and photograph configuration layers (layer arrangement etc.), and a list, or an additive for processing, it is the Europe patent EP 0,355,660A2. What was mentioned to the thing indicated by the description of a number, JP,2-33144,A, and JP,62-215272,A or the following table 1 is used preferably.

[0115]

[A table 1]

(表1)

添加剤の種類	RD17643	RD18716	RD307105
1. 化学増感剤	23頁	648頁右欄	866頁
2. 感度上昇剤		648頁右欄	
3. 分光増感剤	23~24頁	648頁右欄	866~868頁
強色増感剤		~ 649頁右欄	
4. 増白剤	24頁	647頁右欄	868頁
5. 光吸収剤、 フィルター	25~26頁	649頁右欄 ~ 650頁左欄	873頁
染料、紫外 線吸収剤			
6. バインダー	26頁	651頁左欄	873~874頁
7. 可塑剤、 潤滑剤	27頁	650頁右欄	876頁
8. 塗布助剤、 表面活性剤	26~27頁	650頁右欄	875~876頁
9. スタチック 防止剤	27頁	650頁右欄	876~877頁
10. マット剤			878~879頁

[0116] Application to the development of the silver halide color photography sensitive material which contains the pyrrolo triazole derivative of a publication as a cyan coupler especially in official reports, such as JP,5-150423,A, 5-255333, 5-202004, 7-048376, and 9-189988, is effective. The cyanogen coloring matter obtained from a pyrrolo triazole derivative has the outstanding hue, but on the other hand it has the fault which is easy to produce color mixture and a stain, and tends to receive the effect of the stability of a developer with the passage of time. The color development agent constituent of this invention has an advantage of a pile in a lifting in color mixture or a stain, when a pyrrolo triazole derivative is applied to the development of color photography sensitive material made into a cyan coupler. However, the sensitive material which, of course, contained cyan couplers other than a pyrrolo triazole mold coupler can also apply the approach of this invention.

[0117] It is desirable to use together a color image shelf-life amelioration compound like a publication on the Europe patent EP 0,277,589A No. 2 descriptions with a pyrazolo azole coupler, and the above-mentioned pyrrolo triazole coupler and an acyl acetamide mold yellow coupler in the sensitive material for [ of this invention ] application.

[0118] Moreover, it is good even if the cyan coupler of a publication uses [ JP,2-33144,A, the Europe patent EP 0333185A No. 2, JP,64-32260,A, the Europe patent EP 0456226A No. 1 description, the Europe patent EP No. 0484909, the Europe patent EP No. 0488248 description, and EP / 0491197A No. 1 ] it for everything but a phenol mold coupler which was indicated by the well-known reference of the aforementioned table, or a naphthol mold coupler as a cyan coupler.

[0119] As a Magenta coupler used for this invention, the international disclosure WO 92/No. 18901 and a this WO 92/No. 18902 and this WO [ 92/No. 18903 ] publication in everything but 5-pyrazolone system Magenta coupler which was indicated by the well-known reference of the aforementioned table thing is also desirable. although a well-known pyrazolo azole mold coupler is used for this invention besides these 5-pyrazolone Magenta couplers -- inside -- points, such as a hue, image stability, and color enhancement, -- JP,61-65245,A, JP,61-65246,A, JP,61-14254,A, and the Europe patent 226,849th -- No. A -- said -- the 294,785th -- the activity of the pyrazolo azole coupler of a publication is [ of No. A ] desirable.

[0120] although a well-known acyl acetanilide mold coupler is preferably used as a yellow coupler -- inside -- Europe patent EP0447969A No., JP,5-107701,A, JP,5-113642,A, and Europe patent EP-0482552A No. -- said -- the coupler of a publication is preferably used for EP-0524540A No. etc.

[0121]

[Example] Hereafter, although an example explains the mode and effectiveness of this invention further, this invention is not limited to this.

[0122] The plastics bottle was fabricated as follows as a shaping development agent constituent container of an example-11. container and a container. That is, after [ injection ] hollow blow molding of the body part of a bottle is carried out, it is manufactured, and after injection molding a cap part, it made the amount of [ of a cap ] opening carry out heat adhesion of the sheet.

- The body of a configuration bottle is a prism form of appearance 77mmx77mmx301mmH shown in drawing 6, and is a container which prepares the circular regio oralis of 30mmphi in the upper part of the pillar-shaped section, and has been extracted from the upper bed of the pillar-shaped section to the regio oralis, covering. The content volume is 1400ml and the fill of a solution is 1300ml.

- For the high density polyethylene B161 (consistency 0.956) by Asahi Chemical Industry Co., Ltd., and a cap, similarly, the body of [container with which the body of a construction material container and the cap used HDPE is J751A(consistency 0.952)].

[0123] - The average thickness for a wall of the thickness container of a container was changed to five kinds, as shown in the following table, and it was filled up with 1300ml of developer constituents into this. The oxygen transmission rate of each container and the amount of oxygen transparency per 1l. of constituents with which it was filled up were also shown in the following table 2.

[0124] In addition, in a table 2, the measuring method of an oxygen transmission rate is as follows. Namely, nitrogen gas was enclosed in the container, the cap was shut, and after placing for 24 hours into the pure oxygen adjusted to 25-degreeC, 50%RH (relative humidity), and one atmospheric pressure, the oxygen transmission rate was computed by having measured the oxygen density in a container by the gas chromatograph by having used the TCD heat-conduction type detector as the detector.

[0125]

[A table 2]

(表 2)

容器番号	平均厚み	容器の酸素透過速度	充填物 1 ℥当たりの酸素透過速度
	(mm)	(ml/24hrs. atm)	(ml/24hrs. atm 1)
1	0.2	24.0	18.5
2	0.3	16.3	12.5
3	0.5	9.0	6.9
4	0.7	5.7	4.4
5	0.9	4.9	3.8

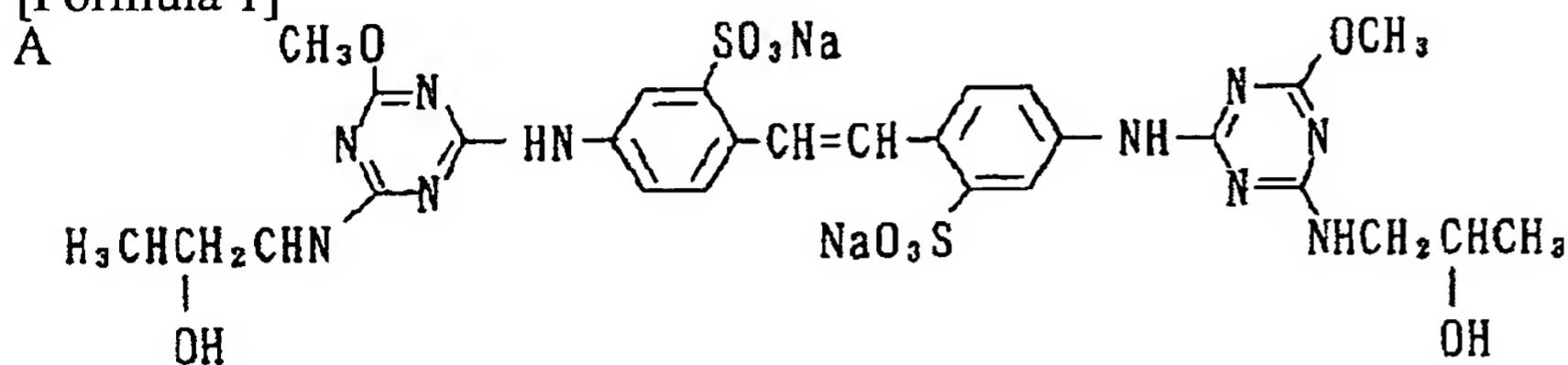
[0126] 2. preparation of a color development agent constituent -- the color development agent constituent of a formula shown below was prepared.

(1) Criteria formula of a color development agent constituent Fluorescent brightener A (following) 12.0 g Fluorescent brightener B (following) 12.0 g Dimethylpolysiloxane system surfactant 0.35g (silicone

KF351A / made in Shin-Etsu Chemical Co., Ltd.)

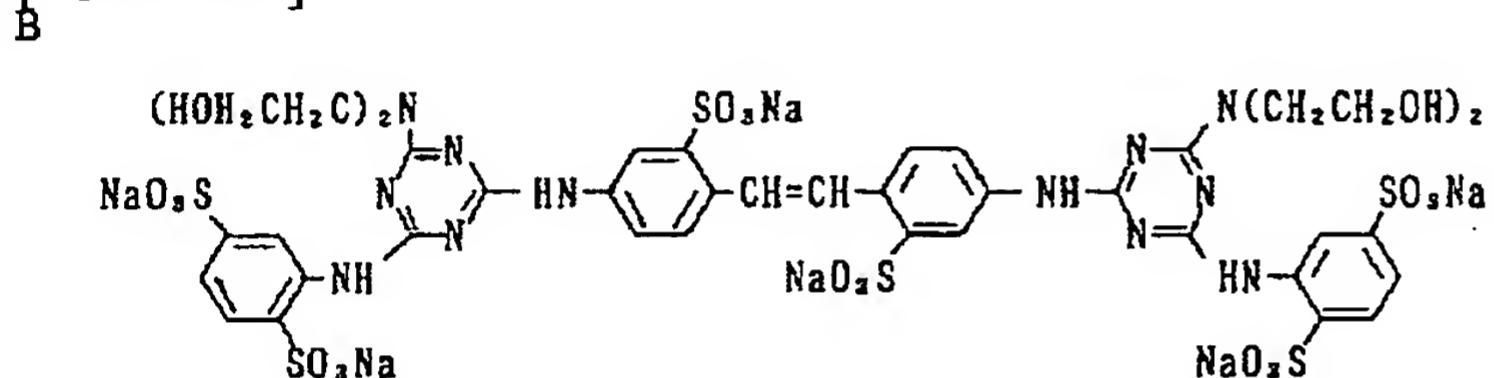
Ethylenediaminetetraacetic acid 15.0 g Disodium - N, N - Screw (sulfonate ethyl) hydroxylamine 30.0 g Tori (isopropanol) amine 30.0 g Potassium hydroxide 18.5 g Sodium hydroxide 24.0 g Sodium sulfite 0.60g Potassium bromide 0.04g Polyethylene glycol 400 30.0 g 4-amino-3-methyl-N - An ethyl-N - (beta-methane sulfo amide ethyl) aniline -3-/disulfuric acid monohydrate and a mono-hydrate 60.0 g Potassium carbonate 100.0 g pH 13.0 Water is added and it is the whole quantity. 1 Liter [0127]

[Formula 1]



[0128]

[Formula 2]



[0129] (2) Fluctuating the amount of components of all the constituents of the formula above-mentioned criteria formula of the color development agent constituent used for the trial by the same ratio, as shown in the following table 3, the component ratio was the same and prepared seven kinds of constituents for a trial with which specific gravity values differ.

[0130]

[A table 3]

(表 3)

組成物番号	成分比 (試験处方 / 基準处方)	比重	p H
①	1 / 1. 3	1. 1 3 8	1 2. 8
②	1 / 1. 2	1. 1 5 0	1 2. 9
③	1 / 1	1. 1 8 0	1 3. 0
④	1 / 0. 9	1. 2 0 0	1 3. 1
⑤	1 / 0. 7 2	1. 2 5 0	1 3. 3
⑥	1 / 0. 6	1. 3 0 0	1 3. 4
⑦	1 / 0. 5 5	1. 3 2 7	1 3. 5

[0131] 3. Each of five kinds of HDPE containers stated to restoration of a color development agent constituent and the stability test above 1 with the passage of time was filled up with every 1300ml each of seven kinds of color development agent constituents shown in the above 2, and the constituent restoration container of a total of 35 (7x5) classes was prepared. 30-degreeC after shutting the cap of the prepared color development agent constituent container -- the constant temperature of 60% of relative humidity RH -- it saved six months each in the constant humidity chamber. It is disodium of each color development agent constituent sample after that. - N, N - The survival rate over initial concentration was computed by having measured the concentration of a screw (sulfonate ethyl) hydroxylamine by the high-speed liquid chromatograph. Disodium - N, N - Screw (sulfonate ethyl) hydroxylamines are the preservatives of this constituent, and it is shown that that a survival rate is high has little degradation of

the color development agent constituent under preservation. In this test condition, it is judged that it has the preservation stability which can use 85% or more of survival rates. The preservatives survival rate of 35 kinds of samples is shown in the following table 4. In addition, it is the range of this invention which was underlined among the table.

[0132]

[A table 4]

(表4)

発色現像剤 組成物		①	②	③	④	⑤	⑥	⑦
容器	比重	1.138	1.150	1.180	1.200	1.125	1.300	1.327
番号	1リットル当りの 酸素透過量							
1	18.5	28%	29	31	32	31	29	23
2	12.5	52	87	89	87	85	85	49
3	6.9	73	89	92	91	86	86	71
4	4.4	82	90	93	92	87	87	81
5	3.8	88	90	93	92	88	88	86

[0133] Although a survival rate is 85% or more and, as for each sample by which the specific gravity of a constituent and the conditions of a container go into the field of this invention, showed sufficient preservation stability, as for the thing of specific gravity higher than this range, the thing of low specific gravity, or what has a large oxygen transmission rate, preservation stability has not reached practical use level. Moreover, although preservation stability is enough though the thing with thick container thickness which has an oxygen transmission rate smaller than the range of this invention is natural, it cannot be overemphasized that it is inferior that container thickness is thick beyond the need in respect of handling nature, the reduction nature (crush) in the recycle process of a used container, and the profitability of an ingredient.

[0134] Example -2 this example shows the example which adjusted specific gravity in the range of this invention with the amount of the mineral salt of an addition component.

1. As a container which satisfies the requirements for container this invention, the container (oxygen transmission rate 6.9 ml/24hrs.atm.l) of the container number 3 of an example 1 was used.

[0135] 2. Preparation of Color Development Agent Constituent (per Container Fill)

As a processing agent constituent for a trial, as shown below based on the conditions (the component ratio of a test formula / criteria formula is 1/1.3) of \*\* of an example 1, the constituent with which compound addition for specific gravity accommodation is performed, and specific gravity values differ was prepared.

[A formula of the color development agent constituent used for the trial]

Fluorescent brightener A (it indicates in the example 1) 12.0 g Fluorescent brightener B (it indicates in the example 1) 12.0 g Dimethylpolysiloxane system surfactant 0.35g (silicone KF351A / made in Shin-Etsu Chemical Co., Ltd.)

Ethylenediaminetetraacetic acid 15.0 g Disodium - N, N - Screw (sulfonate ethyl) hydroxylamine 30.0 g Tori (isopropanol) amine 30.0 g Potassium hydroxide 18.5 g Sodium hydroxide 24.0 g Sodium sulfite 0.60g Potassium bromide 0.04g Polyethylene glycol 400 30.0 g 4-amino-3-methyl-N - An ethyl-N - (beta-methane sulfo amide ethyl) aniline -3-/disulfuric acid monohydrate and a mono-hydrate 60.0 g Potassium carbonate 100.0 g Potassium acetate Table 5 reference pH 13.0 Water is added and it is the whole quantity. 1.3 Liter [0136]

[A table 5]

(表5)

試料番号	⑧	⑨	⑩	⑪	⑫
酢酸カリウム(g/リットル)	0	16	55	159	237
比重	1.138	1.150	1.180	1.260	1.320
保恒剤残存率(%)	73	90	92	89	72
液状	褐色 (強い)	微黄色 (透明)	微黄色 (透明)	微黄色 (透明)	異油状の 浮遊物
備考	比較例	本発明	本発明	本発明	比較例

[0137] In a table 5, sample \*\* is the same as formula value \*\* shown in the example 1. According to the amount of the added potassium acetate, the specific gravity value is increasing other samples.

[0138] 3. Fill Up HDPE Container of Container Number 3 with Every 1300ML Each of Five Kinds of Constituents Stated to Test above 2 of Restoration Sample of Color Development Agent Constituent with the Passage of Time. It saves six months each in a constant humidity chamber. the example 1 after shutting the cap of a container -- the same -- 30-degreeC -- the constant temperature of 60% of relative humidity RH -- Disodium of each color development agent constituent sample in a retention period - N, N - The survival rate over initial concentration was computed by having measured concentration change of a screw (sulfonate ethyl) hydroxylamine by the high-speed liquid chromatograph. The preservatives survival rate of each sample is also shown in a table 5.

[0139] 4. Although a survival rate is 85% or more and each sample by which the specific gravity value of a result constituent goes into the field of this invention showed sufficient preservation stability, \*\* with specific gravity lower than (12) and a degree with specific gravity higher than the upper limit of this range has not reached the usable level whose survival rate is 85%.

[0140] Example -3 this example shows the effectiveness of an addition component with desirable adding further to the color development constituent of this invention.

1. As a container which satisfies the requirements for container this invention, the container (oxygen transmission rate 6.9 ml/24hrs.atm.l per 1L. of content liquid) of the container number 3 of an example 1 was used.

[0141] 2. preparation of a color development agent constituent -- the color development agent constituent of a formula shown below was prepared.

[A formula of the color development agent constituent used for the trial]

Fluorescent brightener A (it indicates in the example 1) 12.0 g Fluorescent brightener B (it indicates in the example 1) 12.0 g Dimethylpolysiloxane system surfactant 0.35g (silicone KF351A / made in Shin-Etsu Chemical Co., Ltd.)

Ethylenediaminetetraacetic acid 15.0 g Disodium - N, N - Screw (sulfonate ethyl) Hydroxylamine 30.0 g Alkanolamine Table 6 reference Potassium hydroxide 18.5 g Sodium hydroxide 24.0 g Sodium sulfite 0.60g Potassium bromide 0.04g Polyethylene glycol Table 6 reference 4-amino-3-methyl-N-ethyl-N - ( [ beta-methane sulfo ] Amide ethyl aniline -3-/disulfuric acid monohydrate and mono-hydrate 60.0 g Potassium carbonate 100.0 g pH 13.0 Water is added and it is the whole quantity. 1 Liter [0142]

[A table 6]

(表6)

試料番号	添加物		経時安定性	
	化合物	(g/リットル)	保恒剤 残存率(%)	白地部濃度増加 ( $\Delta D_B$ )
⑯	—	—	85	0.01
⑯	トリイソプロピルアミン	(30)	91	0.003
⑯	ジエタノールアミン	(30)	89	0.005
⑯	ポリエチレングリコール 分子量100	(30)	87	0.007
⑯	同 上 分子量400	(30)	89	0.005
⑯	同 上 分子量1500	(30)	88	0.008
⑯	トリイソプロピルアミン (ポリエチレングリコール 分子量400)	(30)	92	0.001

[0143] In a table 6, a sample (13) is a formula which does not contain all the addition compounds of a publication in a table 6 in the above-mentioned formula, and sample (14) - (19) adds the additive of table 6 publication to this formula. A sample (19) is the criteria formula used in the examples 1 and 2.

[0144] 3. Fill Up HDPE Container of Container Number 3 with Every 1300Ml Each of Seven Kinds of Constituents of Test Report 6 of Restoration Sample of Color Development Agent Constituent with the Passage of Time. It saves six months each in a constant humidity chamber. the example 1 after shutting the cap of a container -- the same -- 30-degreeC -- the constant temperature of 60% of relative humidity RH -- Disodium of each color development agent constituent sample in a retention period - N, N - The survival rate over initial concentration was computed by having measured concentration change of a screw (sulfonate ethyl) hydroxylamine by the high-speed liquid chromatograph. The preservatives survival rate of each sample is also shown in a table 6.

[0145] 4. The development followed down stream processing which this also shows later, using a color paper sample (FUJIKARA paper SUPER[ by Fuji Photo Film Co., Ltd. ] FA9) as a photograph sex-test sensitive material. While diluting each of color development agent constituent sample (13) - (19) 4 times with water, preparing the replenisher in the developer and performing 25% of water dilution to this further, the 10g [1. ] sodium chloride was added, pH was adjusted to 10.2 with the sulfuric acid, and the developer was prepared, and negatives were developed, filling up the replenisher which fills each developer to the developer tank of the small developing machine for an experiment, and corresponds at it. This also performed the development according to the development approach shown later.

Assessment of a photograph property was performed by developing negatives, respectively with the developer prepared by the constituent sample which carried out the passage of time to the developer made from the constituent before the trial of color development agent constituent (13) - (19) with the passage of time, and investigating change of the photograph nature under trial with the passage of time. The change value of the white stain in the passage of time, i.e., the change value of the blue filter light reflex concentration value (it abbreviates to DB) of the unexposed section, was used as a rule of thumb of the stability of a photograph property.

[0146] 5. The result test result was also collectively shown in a table 6. A preservatives survival rate is 85% or more, and the increment in a white concentration value is also 0.01 or less, and each sample fulfills practical use conditions. In addition, the practical limit of the increment in the white concentration value in this test condition is 0.02. It was shown by addition of alkanolamine and a polyethylene glycol by the comparison with a sample (13) that effectiveness increased further that a constituent is further stable and by using combining them. Moreover, it was shown that tri-isopropanolamine is excellent in alkanolamine and the thing of molecular weight 400 is also excellent in a polyethylene glycol.

[0147] [The photograph characteristic test approach]

(1) Development process [0148]

Down stream processing \*\* Whenever At the time Between Amount of supplements \* color development 38.5 degrees C 45 seconds 45ml bleaching fixation 38.0 degrees C 45 seconds 35ml rinse (1) 38.0 degrees C 20 seconds - Rinse (2) 38.0 degrees C 20 seconds - rinse (3) \*\*38.0 degree C 20 seconds - rinse (4) \*\*38.0 degree C 20 seconds 121ml desiccation 80 \*\* 30 seconds (notes)

\* Sensitive-material 1m2 per -- a supplement -- a rinse (3) is equipped with rinse cleaning system RCby amount \*\* Fuji Photo Film Co., Ltd.50D, a rinse is taken out from a rinse (3), and it sends to a reverse osmosis module (RC50D) with a pump. The permeated water obtained by this tub is supplied to a rinse (4), and retentate is returned to a rinse (3). The water permeate flow to a reverse osmosis module is 50-300ml. Pumping pressure was prepared and temperature control circulation was carried out for 10 hours on the 1st so that a part for /might be maintained. The rinse was made into 4 tank counterflow method from (1) to (4).

[0149] (2) The test fluid of entering [ which was stated to the above 2-4 ] a container with the passage of time and the newly prepared constituent were used for a color development replenisher and tank liquid among processing \*\*\*\* processing liquid, and the bleach fix bath and the rinse used the thing of the next formula.

[0150]

[Bleach fix bath] [Tank liquid] [Replenisher]

Water 800ml 800ml ammonium thiosulfate (750g/(1.))

107.0ml 214.0ml m-carboxymethyl benzenesulfonic acid 8.3g 16.5g ethylenediaminetetraacetic acid iron (III) ammonium 47.0g 94.0g ethylenediaminetetraacetic acid 1.4g 2.8g nitric acid (67%) 16.5g 33.0g imidazole 14.6g 29.2g ammonium sulfite 16.0g 32.0g potassium metabisulfite 23.1g 46.2g water is added. 1000ml 1000ml pH (25 degrees C / acetic acid, and ammonia adjust)

6.5 6.5 [0151]

[Rinse] [Tank liquid] [Replenisher]

Chlorinated-isocyanuric-acid sodium 0.02g 0.02g deionized water (5 or less second/cm of conductivity)

1000ml 1000ml pH 6.5 6.5 [0152]

[Effect of the Invention] By adjusting the specific gravity value of the color development agent constituent of 1 agent configuration, and the oxygen transmission rate of a container in the respectively fixed range Become possible to save a color development agent constituent at stability using the large polyolefine container (especially HDPE) of oxygen permeability originally, therefore the playback activity of a container is possible in respect of environmental protection. A development working plane can also be simple for preparation of a processing agent constituent to a replenisher, and its handling nature can be good, and it can be maintained to stability also in respect of the photograph engine performance. Moreover, the stability of a developer constituent increases further by adding the alkanolamine of polyalkylene glycols, such as a polyethylene glycol, and a general formula (A) in a constituent.

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[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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## DESCRIPTION OF DRAWINGS

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### [Brief Description of the Drawings]

[Drawing 1] It is the outline block diagram showing the printer processor as which one example of the development approach using the developer constituent of this invention was adopted.

[Drawing 2] It is the strabism which shows the printer processor as which one example of the development approach using the developer constituent of this invention was adopted.

[Drawing 3] It is a front view near the loading section.

[Drawing 4] It is a side elevation near the loading section.

[Drawing 5] It is the decomposition perspective view of the container for developer constituents concerning 1 operation gestalt of this invention.

[Drawing 6] It is drawing showing the container for developer constituents concerning the gestalt of 1 operation of this invention.

### [Description of Notations]

73 Sensitive-Material Throughput Detection Means

122 Display (Alarm Means)

300 Restoration Section

1300 Bottle (Container for Photographic-Processing Agents)

1302 Body of Container

1304 Male Screw (Screw Section)

1308 Polyethylene Sheet (Sheet Member)

1310 Cap (Holdown Member)

1312 Pars Basilaris Ossis Occipitalis

1314 Opening

N The negative color film developed negatives

P Color paper

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[Translation done.]